

Lecture 10. Vibrational chemical reactions.

The purpose of the lecture: to provide information on vibrational chemical reactions and their features.

Expected results: students receiving information on vibrational chemical reactions and their differences from ordinary reactions.

Vibrational chemical reactions are certainly of interest both for chemical technology and for biological processes, for example, biorhythms or cell division, etc.

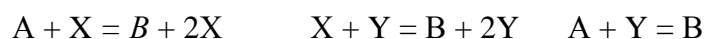
Oscillations are always associated with some kind of non-linearity and feedback - positive or negative.

Chemical vibrations can be caused either by features (non-linearity, autocatalysis by intermediate products, branched chain reaction, etc.) of chemical kinetics and are observed under isothermal and spatially uniform conditions of closed systems, either due to heat generation in an exothermic process (positive feedback), or open systems with continuous supply of reagents.

For example, in the presence of a lower limit in the oxidation of phosphorus, the inlet of a reagent into a vessel leads to a gradual increase in concentration, reaching the limit, and then quickly and completely burn out. After which the situation can be repeated many times, which was observed experimentally by many researchers. Frank-Kamenetsky gave this process a good analogy - a vessel that gradually fills with water and capsizes at a certain degree of filling. In such a process, neither the amplitude nor the frequency depend on the chemical kinetics itself.

The role of positive feedback can be played by temperature in the exothermic reaction, even if the reaction itself is simple. In an open system, the gradual accumulation of reagents will lead to a nonlinear increase in temperature and rapid burnout of the reagents, then the cooling of the system and the repetition of the cycle with further filling.

Now we show a variant of a purely chemical vibration, following Frank-Kamenetsky. In the oxidation of higher hydrocarbons, two intermediate products (peroxides and aldehydes) catalyze (accelerate) the process. Conditionally, the scheme is as follows:



The system of kinetic equations has the form:

$$\frac{dx}{dt} = k_1 ax - k_2 xy$$
$$\frac{dy}{dt} = k_2 xy - k_3 ay$$

If we take into account the quasistationary nature of the intermediate products and conduct an analysis in a linear approximation of deviations from the stationary state, then we obtain:

$$x_0 = \frac{k_3 a}{k_2} \quad \text{and} \quad y_0 = \frac{k_1 a}{k_2} \quad \text{stationary concentrations.}$$

$$x = x_0 + \eta \quad \text{и} \quad y = y_0 + \vartheta \quad \text{- current concentrations of intermediates.}$$

We obtain a linearized system of equations:

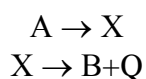
$$\frac{d\eta}{dt} \approx -k_3 a \vartheta ; \quad \frac{d\vartheta}{dt} \approx k_1 a \eta$$

which boils down to the following:

$$\frac{d\eta}{dt} \approx -k_1 k_3 a^2 \eta$$

The solution to the last equation is sinusoidal oscillation.

Thus, an explanation was obtained for the so-called outbreaks of cold (almost isothermal) flame during the oxidation of hydrocarbons. Another example of purely kinetic chemical vibrations is the famous Belousov-Zhabotinsky reaction — the oxidation of organic acids (for example, citric) and their esters by bromate in an acidic medium, catalyzed by cerium ions. Finally, it is worth considering an example of temperature-kinetic vibrations in an ideal mixing reactor that is important for chemical technology. A similar system of kinetic equations is obtained for a closed system, but more complex kinetics of two consecutive reactions:



If we assume that heat is released only in the second stage, the second reaction has a large activation energy and there is little intermediate product, then the equations coincide:

$$\begin{aligned} \frac{dx}{dt} &= k_1 C - k_2 x \equiv \Phi(x, T) \\ \frac{dT}{dt} &= \frac{Q}{c_p \rho} k_2 x - \frac{\alpha S}{c_p \rho w} (T - T_0) \\ k_2 &= A \exp\left(-\frac{E}{RT}\right) \end{aligned}$$

The nature of the possible oscillations can be explained on the Semenov diagram. For small x , the temperature differs little from T_0 and k_2 is small and x accumulates and is almost not consumed. For a certain x^* , the condition of thermal explosion can be fulfilled (the heat release curve $k_2 X$ from T concerns the direct heat sink), the flow rate x increases sharply and the intermediate product burns out. Then the system is cooled and the cycle repeats.

An experimental study of the vibrational mode of butane oxidation

To study the oxidation of butane, a flat flame reactor was used, where the sections are connected by a flat perforated plate.

Using the ESR method for these purposes is impossible due to the inertia of the method. To study the behavior of radicals, the differential thermocouple method was used. One of the thermocouples included differentially was coated with a solution of LiCl in ethyl alcohol.

Visual observations conducted in the dark with a pale blue glow of low intensity show that the flame front is a horizontally located disk 1-2 mm thick, the distribution of which is complex. A flat, slightly luminous disk moves from top to bottom with acceleration to a certain point, then the direction of movement changes.

A flat, light-luminous disk moves from top to bottom with acceleration, reaching a certain point, then the direction of movement changes; this changes the shape of the luminous zone, which is half the pseudosphere with the axis coinciding with the axis of the second section of the reactor. Previously, a model was proposed that represented the oscillation regime as a result of two successive events: 1) the degenerate branching reactions leading to an increase in temperature and the appearance of a flame front, and 2) the propagation of the flame front in the direction of the fresh mixture with the release of thermal energy. Thus, in the oscillatory regime of thermocouples,

the periodic propagation of the flame front is recorded. It is clear that the sensitivity of the method is insufficient to determine the concentration of radicals during slow oxidation. On the oscillogram of stable oscillations, two peaks can be distinguished: the first corresponds to the propagation of the flame front down, the second to the propagation of the flame front up. Signals from the differential thermocouple recorded two local minima and one maximum peak. At the beginning, the oscillogram of damped oscillations does not differ from the oscillogram of stable oscillations, but with time the local minimum gradually disappears and the amplitude of the oscillations increases relative to the zero differential thermocouple. At the same time, the temperature line reaches a threshold value. In the stationary mode of low-temperature combustion, the lines and smoothly reach their upper limit.

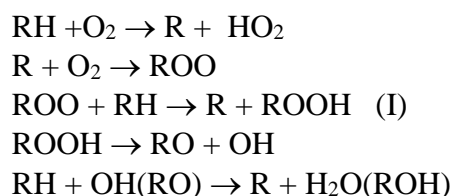
In order to better understand the nature of oscillation processes, it is advisable to study the behavior of radicals.

The presence of local minima on the curve of changes in the concentrations of active particles can be explained by the desorption of particles previously adsorbed on the surface of a thermocouple junction treated with LiCl. To confirm this assumption, an experiment was conducted in which the differential thermocouple was heated (until the flame front approached) to the front temperature. When the thermocouple is heated by electric current, the signal changes qualitatively, the minima disappear and two distinct maxima are observed, i.e. As expected, when the thermocouple is heated, particles are desorbed from the surface of the thermocouple.

The phase portrait of the system in coordinates, the amplitude of temperature fluctuations - the relative concentration of radicals in the case of stable vibrations or a limit cycle is a closed curve of complex shape. With unchanged parameters, the system in the stable oscillation mode passes successively the whole set of points of this closed curve for an arbitrarily long time. Thus, in various modes of cold-flame oxidation of butane, a periodic change in the concentration of radicals is observed, due to the periodic propagation of the flame front through the combustible mixture. It is shown that the propagation velocity of a cold flame varies along the length of the reactor and passes through a maximum.

The lack of information about the detailed kinetics of oxidation of the process under consideration, on the one hand, and the difficulty of using detailed schemes for analyzing the basic laws of flame propagation (burning rate, dependence on the mixture composition, pressure, etc.), on the other hand, necessitate the use of simplified empirical chemical schemes turning into a flame. In this regard, the numerical simulation of the problem is carried out with the following two-stage mechanism of low-temperature oxidation of the combustible mixture, similar to the Salnikov scheme.

The concentration of hydrocarbon in the mixture as a result of cold flame oxidation in the second section, followed by chain extension and degenerate branching of the alkyl hydroperoxide in the flame front during reactions



decreases (accordingly, the concentration of hydrocarbon radicals increases). As the concentration of radicals and the temperature of the mixture increase in the second section, at the same time as reactions (I), exothermic reactions of the death of hydrocarbon radicals begin with partial formation of stable products:



We denote by Y_1 and Y_2 the mass concentrations of hydrocarbon and their radicals in the mixture, and by

$$W_1 = k_1 Y_1 = Y_1 k_{10} \exp\left(-\frac{E_1}{RT}\right)$$

$$W_2 = k_2 Y_2 = Y_2 k_{20} \exp\left(-\frac{E_2}{RT}\right)$$

accordingly, the mass rate of their decrease in the reactor as a result of reaction (I) and (II).

Literature

1. Mansurov Z.A. Cool sooting flames of hydrocarbons//J. of Thermal Science, 2001. – Vol. 10, № 3. – P. 269-280.
2. Гарел Д., Гарел О., Колебательные химические реакции. М.: Мир, 1986.
3. Жаботинский А.М. Концентрационные колебания. М.: Наука, 1974.
4. Мансуров З.А., Калтаев А., Шакибаев Н. Экспериментальное исследование колебательного режима окисления бутана // Химическая физика, № 3, 1999, с.79.